# Mass Transfer in Low-Density Xerogel Catalysts

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*Texture and morphology of a Pd-Ag/$SiO_2$ hydrodechlorination low-density xerogel catalyst prepared by a cogelation sol-gel process were characterized in detail to examine mass transfer in such catalysts. The catalyst consists of active Pd-Ag nanocrystallites trapped inside elementary 20 nm microporous silica particles arranged in larger aggregates, which constitute the macroscopic pellet. To reach active sites, reactants must first diffuse through large pores located between aggregates of $SiO_2$ particles and then through smaller pores located between those elementary particles inside the aggregates. Finally, they diffuse through micropores located inside silica particles. Diffusion in such a "funnel" structure cannot be described assimilating the pellet to a pseudo-continuum. Diffusion should be examined carefully at three levels of decreasing size: the macroscopic pellet, the aggregate of silica particles, and the elementary silica particle. This approach shows that cogelled xerogel catalysts have remarkable mass-transfer properties.*

## Introduction

In a heterogeneous catalytic process, the reactants must diffuse from the bulk of the fluid phase to the surface of the catalyst pellets, and then from that surface to the active sites through the porous structure of the pellet. They react on the active sites and the products formed must diffuse in the opposite direction. Therefore, such a process involves both physical steps (diffusion) and chemical steps (reaction). Depending on the relative rates of those various steps, the overall rate of the process is governed by the physical kinetics or by the chemical kinetics (Satterfield, 1970; Carberry, 1987; Villermaux, 1993; Emig and Dittmeyer, 1997). In order to study mass transfer inside a porous catalyst, the catalyst pellet is often regarded as a pseudo-continuum, that is, a pseudo-homogeneous medium in which the diffusion of a gaseous species is described by the same single effective diffusion coefficient everywhere inside the pellet the size of which corresponds to the length scale for diffusion (Satterfield, 1970; Carberry, 1987; Villermaux, 1993; Emig and Dittmeyer, 1997; Froment and Bischoff, 1990; Kapteijn and Moulijn, 1997). However, in some cases, it seems unreasonable to assume that catalyst pellets are pseudo-homogeneous media. In a study on the polymerization of olefins on heterogeneous Ziegler catalysts, McKenna et al. (1999) conclude that the pseudo-homogeneous pellet concept does not apply to the whole pellet, but rather to small zones inside the pellet. According to this view, the pellet is composed of pseudo-homogeneous zones corresponding to a diffusion length scale which is significantly lower than its macroscopic size.

In a previous article (Heinrichs et al., 1997a), low-density Pd-Ag/$SiO_2$ xerogel catalysts were synthesized by a sol-gel procedure in which the preparation of the support and the distribution of the active metals precursors in its porosity are gathered in a single step. Those catalysts are composed of active Pd-Ag nanocrystallites ($\leq 3$ nm) trapped inside 10 to 20 nm microporous silica particles, which are arranged in larger aggregates. They have been developed to convert selectively chlorinated alkanes into alkenes, particularly 1,2-dichloroethane ($ClCH_2$-$CH_2Cl$) into ethylene (Heinrichs et al., 1997a; Heinrichs, 1999; Delhez et al., 2000).

The very particular texture and morphology of those cogelled xerogel catalysts does not allow the use of the pseudo-homogeneous concept for the whole pellet. The aim of this article is to show, through a detailed textural and morphological characterization and through adequate local diffusion calculations, that the hierarchical structure of those catalysts leads to remarkable mass-transfer properties avoiding diffusional limitations.

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## Experimental Methods

### *Catalyst preparation and characterization*

The catalyst used in this study is a 1.9%Pd-3.7%Ag/$SiO_2$ xerogel prepared by a one-step sol-gel procedure and characterized by nitrogen adsorption, mercury porosimetry, helium pycnometry, electron microscopy, X-ray diffraction, inductively coupled plasma atomic emission spectroscopy, and CO chemisorption. Details about synthesis procedure and characterization methods can be found elsewhere (Heinrichs et al., 1997a; Heinrichs, 1999; Delhez et al., 2000; Heinrichs et al., 2000).

### *Reaction rate measurement*

The 1,2-dichloroethane apparent consumption rate was measured at 500, 573, and 623 K, which corresponds to the temperature domain of the industrial process (Ito et al., 1994; Schoebrechts and Janssens, 1996; Delhez et al., 2000), and at 2.96 atm in a differential tubular reactor with an internal diameter of $8 \times 10^{-3}$ m. The catalytic bed consists of crushed and sieved catalyst pellets between $250 \times 10^{-6}$ and $500 \times 10^{-6}$ m. Details concerning the experimental device and the reaction rate measurements are given in Heinrichs (1999).

### *Mass-transfer experiments*

Experimental tests for detection of possible external and/or internal diffusional limitations were performed at 573 K and 2.96 atm. For the external diffusion test, three experiments with a catalyst pellet of mean size $375 \times 10^{-6}$ m were performed by simultaneously varying the amount of catalyst and the total flow rate, while keeping the space time constant. For the internal diffusion test, three experiments were performed with $0.0416 \times 10^{-3}$ kg of catalyst pellets and a total flow rate of 0.25 mmol $s^{-1}$ by varying the mean size of the pellets (Table 1).

## Results

### *Texture and morphology of the catalyst*

The internal morphology of the Pd-Ag catalyst pellets is described in Figures 1–5. Figure 1 is a SEM micrograph which gives us an idea of the 3-D morphology of the xerogel at the scale of the micrometer. Figures 2 to 4 are TEM micrographs at growing magnification obtained with slices of the material. At the scale of Figures 1 and 2, the xerogel pellet contains silica aggregates separated by large pores. An approximate quantification based on those two pictures indicates that the size of aggregates, as well as the width of pores between those aggregates, range from several tens to several hundreds of nanometers. The examination of the catalyst at a higher magnification (Figure 3) shows that the silica aggregates are composed of highly interpenetrated elementary $SiO_2$ particles. Due to the high interpenetration of those particles, the accurate measurement of their size is particularly difficult. However, at the periphery of aggregates, that is, in the clear zones of Figure 3, single particles are distinguishable and their size can be evaluated. The size distribution of silica particles is very narrow and measurements on 20 particles indicate that their diameter is close to $20 \times 10^{-9}$ m. Active metal crystallites can be observed at the highest magnifications (Figures 3 and 4). The composition, size, and localization of metal crystallites have been examined in previous articles (Heinrichs et

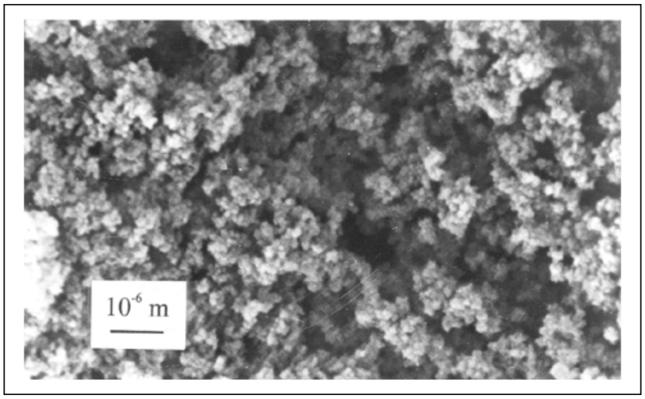

**Figure 1. SEM micrograph of the Pd-Ag xerogel catalyst (original magnification, 16,000).**

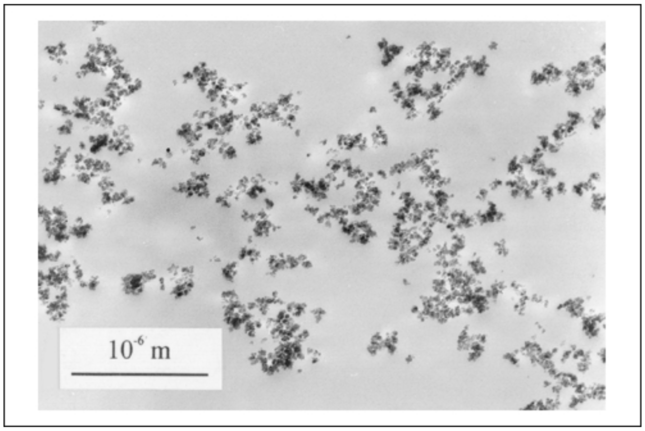

**Figure 2. TEM micrograph of the Pd-Ag xerogel catalyst (original magnification, 40,000).**

**Table 1. Mass Transfer Experiments**

| External Transfer | | | Internal Transfer | |
|---|---|---|---|---|
| Catalyst Mass ($\times 10^{-3} \cdot$ kg) | Inlet Total Flow Rate (mmol$\cdot s^{-1}$) | $ClCH_2$-$CH_2Cl$ Conv. (mol %) | Pellet Mean Size ($\times 10^{-6} \cdot$ m) | $ClCH_2$-$CH_2Cl$ Conv. (mol %) |
| 0.0416 | 0.25 | 6.8 | 187.5 | 7.0 |
| 0.0833 | 0.5 | 6.5 | 375 | 6.8 |
| 0.1665 | 1 | 7.1 | 750 | 7.6 |

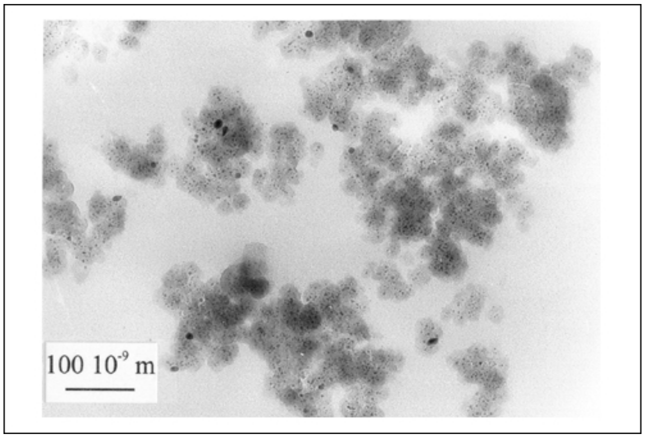

**Figure 3. TEM micrograph of the Pd-Ag xerogel catalyst (original magnification, 200,000).**

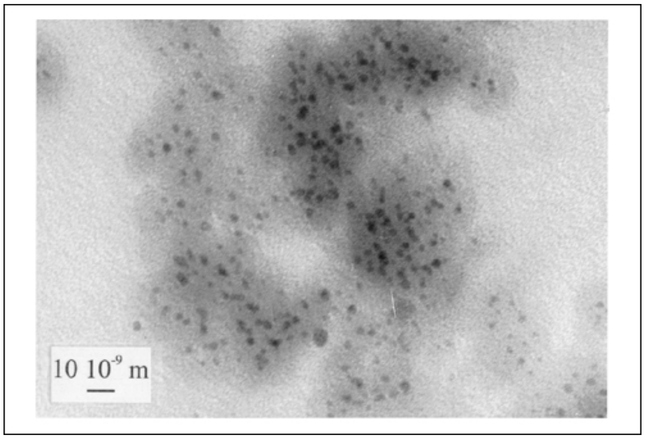

**Figure 4. TEM micrograph of the Pd-Ag xerogel catalyst (original magnification, 800,000).**

al., 1997a, 2000). According to those studies, the few large black points observed in Figure 3 are pure silver crystallites which are inactive for hydrodechlorination. Those crystallites, whose size are around or exceed $10\times10^{-9}$ m, are located outside silica particles. The active metal crystallites are the small black points whose size are around $3\times10^{-9}$ m. Those nanocrystallites are Pd-Ag alloy crystallites having a 54 at.% Pd − 46 at.% Ag bulk composition and a 10 at.% Pd − 90 at.% Ag surface composition. It has been shown that they are located inside the elementary silica particles due to the role of a nucleation agent played by the Pd precursor complexes in the formation of those silica particles (Heinrichs et al., 1997ab; Alié et al., 1999).

The texture examination by $N_2$ adsorption, as well as Hg porosimetry, shows that the Pd-Ag xerogel exhibits a very broad pore width distribution. The cumulated distribution over the complete pore width range accessible with those two techniques is shown in Figure 5. This distribution was obtained by applying a combination of various methods to their respective validity domains and by adding the porous volumes corresponding to those domains (Heinrichs et al., 1997a).

In the micropore domain (width $< 2\times10^{-9}$ m), the xerogel exhibits a very narrow pore width distribution centered on a mean value of about $0.8\times10^{-9}$ m, which corresponds to the steep volume increase followed by a plateau in Figure 5. In the range of meso- and macropores (width $> 2\times10^{-9}$ m), the catalyst exhibits a broad distribution. According to previous studies (Heinrichs et al., 1997ab), the $0.8\times10^{-9}$ m micropores are located inside the $20\times10^{-9}$ m elementary silica particles and the continuous meso- and macropore distribution is located in voids between those $SiO_2$ particles and between aggregates constituted of those particles.

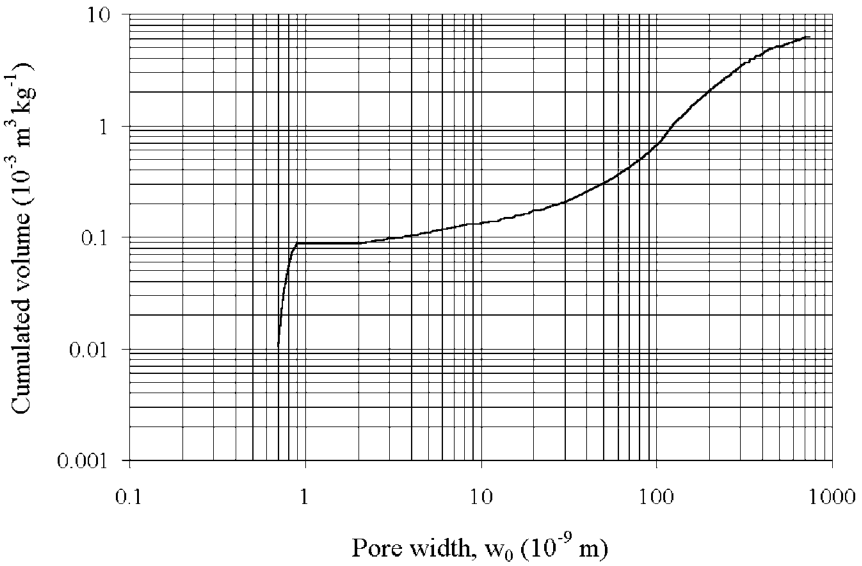

**Figure 5. Pore width distribution of the Pd-Ag xerogel catalyst.**

**Table 2. Weisz Modulus Calculation at 3 Levels and 3 Temperatures**

| | 500 K | 573 K | 623 K |
|---|---|---|---|
| $r$(mmol·kg$^{-1}$·s$^{-1}$) | 0.27 | 1.51 | 7.66 |
| $C_b$ (mmol·m$^{-3}$) | 3,395 | 2,953 | 2,653 |
| $D_m$ (m$^2$·s$^{-1}$) | $3.1\times10^{-5}$ | $3.9\times10^{-5}$ | $4.5\times10^{-5}$ |
| $\Phi_1$ (Pellet) | $2\times10^{-5}$ | $1\times10^{-4}$ | $7\times10^{-4}$ |
| $\Phi_2$ (Aggregate) | $4\times10^{-8}$ | $2\times10^{-7}$ | $1\times10^{-6}$ |
| $\Phi_3$ (Particle) | $7\times10^{-10}$ | $4\times10^{-9}$ | $2\times10^{-8}$ |

It is particularly interesting to note that the total pore volume of this xerogel, which is equal to $6.25\times10^{-3}$ m$^3$ kg$^{-1}$, is in the same order of magnitude as the pore volume of aerogels described in literature (Pajonk, 1991; Pajonk et al., 1997; Rao et al., 1997; Heinrichs et al., 1997ab; Rigacci et al., 1998). For this reason, the Pd-Ag xerogel is called "low-density xerogel." In order to avoid confusion, it is useful at this point to make a brief comment about the word "density". According to IUPAC recommendations for the characterization of porous solids (Rouquerol et al., 1994), three densities can be defined: the true density, the apparent density, and the bulk density. The true density of an object is the density of that object excluding pores; the apparent density of an object is the density of that object including closed pores; and the bulk density of an object is the density of that object including all pores (open and closed). In the "low-density xerogel" appellation, the word density refers obviously to the bulk density of the catalyst pellet. The catalyst apparent density was measured by He pycnometry and the obtained value was $2.22\times10^3$ kg m$^{-3}$. This value is very close to the true density of dried alkoxy-derived silica gels, that is, $2.2\times10^3$ kg·m$^{-3}$ (Yamane, 1988), which means that there are no closed pores inside the catalyst pellets.

### *Apparent reaction rate and mass-transfer experiments*

Experimental values obtained for the apparent reaction rate $r$ are given in Table 2. Results of the experimental tests for detection of possible external and/or internal diffusional limitations are presented in Table 1. The test for external diffusion indicates that the ClCH$_2$-CH$_2$Cl conversion is independent of the total flow rate to within the experimental error, which means that no external diffusional limitations exist (Kapteijn and Moulijn, 1997; L'Homme, 1970). The test for internal diffusion indicates that the ClCH$_2$-CH$_2$Cl conversion is pellet size independent to within the experimental error, which usually means that no internal diffusional limitations exist (Kapteijn and Moulijn, 1997; L'Homme, 1970). However, in the particular case of cogelled xerogel catalysts, the experimental test for internal diffusion presented in Table 1 draws conclusions only for diffusion in very large pores located between silica aggregates in the catalyst pellet, that is, for diffusion from the pellet surface to the aggregate surface. This point is discussed in detail later.

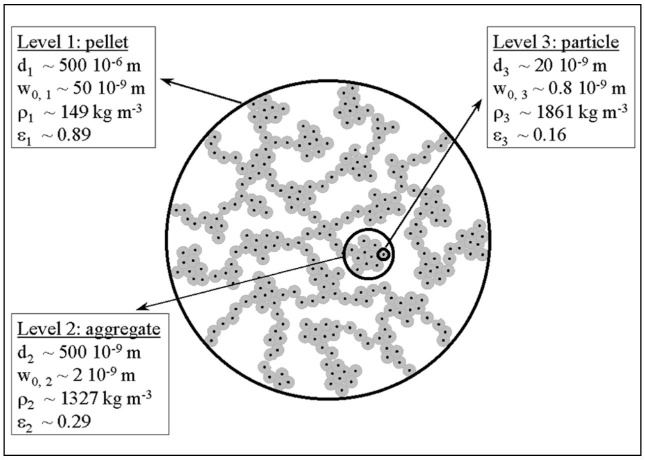

**Figure 6. Texture and morphology of a low-density cogelled xerogel catalyst.**

## Discussion

Results from the analysis of the catalyst texture and morphology indicate that the Pd-Ag xerogel is composed of overlapping entities exhibiting different textures: silica particles are basic blocks which constitute aggregates which themselves constitute the catalyst pellet. In order to reach the active Pd-Ag alloy particles, reactants have to diffuse through a continuous distribution of macro- and mesopores located in voids between aggregates of elementary SiO$_2$ particles and between those elementary particles and then through the 0.8 $\times10^{-9}$ m micropores located inside the elementary SiO$_2$ particles. This situation is illustrated in Figure 6.

In diffusion calculations, the catalyst pellet is often regarded as a pseudo-homogeneous medium in which the diffusion of a species is still described by Fick's law, as in a homogeneous phase, but in which the ordinary fluid molecular diffusivity $D_m$ is replaced by a diffusion coefficient called the effective diffusivity $D_e$ (Satterfield, 1970; Villermaux, 1993; Froment and Bischoff, 1990). The pseudo-homogeneous pellet concept implies that $D_e$ has the same value everywhere inside the pellet and that the length scale for mass transfer corresponds to the pellet size. The effective diffusivity $D_e$ depends, among other things, on morphological properties of the catalyst pellet such as the void fraction and the tortuosity factor, which characterize the tortuous nature of the pores and their constrictions. Moreover, when the Knudsen diffusion becomes significant or even dominant with regard to ordinary gas molecular diffusion (which occurs with pore widths smaller than around $100\times10^{-9}$ m (Weisz, 1973)), the effective diffusivity $D_e$ becomes a function of the pore width (Satterfield, 1970; Villermaux, 1993; Froment and Bischoff, 1990; Weisz, 1973). Various models are presented in literature for the evaluation of $D_e$. In the simplest one, the effective diffusivity is calculated from single mean morphological properties characterizing the catalyst pellet: one void fraction, one tortuosity factor, and one mean pore radius. This model is adequate to describe diffusion in a catalyst having a fairly narrow unimodal pore width distribution (Froment and Bischoff, 1990). When a catalyst exhibits a bimodal pore width distribution, the random pore model of Wakao and Smith (1962) can be successfully used (Satterfield, 1970; Froment and Bischoff, 1990). In this model, the effective diffusivity $D_e$ is calculated from two effective diffusivities which are calculated using one mean macropore radius and one mean micropore radius.

The detailed characterization of the texture and the morphology of the Pd-Ag cogelled xerogel catalyst previously presented, shows that it is unlikely that a pellet of that catalyst should be treated as a pseudo-homogeneous medium in which the diffusion of a species is characterized by a single effective diffusivity $D_e$. It seems ridiculous to calculate an effective diffusivity by using, for example, one or two, as in the model of Wakao and Smith (1962), mean pore width(s) in a porous material which exhibits a distribution ranging from micropores of $0.8 \times 10^{-9}$ m to macropores of several hundred nanometers (Figure 5) (Froment and Bischoff, 1990). Moreover, it also seems unrealistic to use a single void fraction and a single tortuosity factor to calculate a single effective diffusivity $D_e$ since these two morphological properties differ from one scale (silica particle, aggregate, or pellet) to another. In order to study mass transfer in such a medium, we suggest it to be considered at three discrete levels with decreasing sizes: level 1: macroscopic pellet; level 2: aggregate of silica particles; and level 3: elementary silica particle containing an active Pd-Ag alloy crystallite. Each level is assumed to correspond to a pseudo-homogeneous medium with its own size, bulk density, void fraction, tortuosity, and single pore width. At level 1 (pellet), only diffusion of molecules between the external surface of the xerogel pellet and the external surface of the aggregates of silica particles, that is, diffusion in large pores between aggregates, is considered; at level 2 (aggregate), the only diffusion of molecules between the external surface of the aggregate and the external surface of the silica particles, that is, diffusion in pores between $SiO_2$ particles, is considered; at level 3 (particle), only diffusion of molecules between the external surface of the elementary silica particle and the active Pd-Ag alloy crystallite, that is, diffusion inside microporous $SiO_2$ particles, is considered.

At the start of a kinetic study in heterogeneous catalysis, when the intrinsic chemical kinetics is not known, the presence of possible pore diffusion limitations, which could falsify the kinetic measures, is generally examined via the estimation of the Weisz modulus $\Phi$ (Satterfield, 1970; Carberry, 1987; Villermaux, 1993; Emig and Dittmeyer, 1997; Froment and Bischoff, 1990)

$$\Phi = \frac{r \rho L^2}{D_e C_s} \tag{1}$$

This modulus compares the observed reaction rate to the diffusion rate. If $\Phi \ll 1$, there are no pore diffusion limitations and the observed rate $r$ is equal to the intrinsic rate of the chemical reaction. If $\Phi \gg 1$, the observed reaction rate $r$ does not correspond to the intrinsic rate due to diffusional falsifications. As mentioned above, in classical diffusion calculations, the catalyst pellet is regarded as a pseudo-homogeneous medium. With this concept, a single Weisz modulus $\Phi$ is calculated for the whole pellet. Indeed, the pseudo-homogeneity concept implies single morphological properties of the pellet and, therefore, a single effective diffusivity $D_e$ as described earlier, but also a single bulk density $\rho$ is implied for the whole pellet. Moreover, in a pseudo-homogeneous pellet, there is a single characteristic size $L$, that is, a single length scale for mass transfer, which corresponds to the size of the pellet. It has already been explained that the pseudo-homogeneous model is not suitable for cogelled xerogel catalysts and their examination at three discrete levels (pellet, aggregate, particle) has been proposed. Since each level is assimilated to a pseudo-homogeneous medium with its own morphological properties, one level is characterized by its own Weisz modulus

$$\Phi_i = \frac{r \rho_i L_i^2}{D_{e,i} C_{s,i}} \tag{2}$$

where the subscript $i$ refers to the level ($i = 1$: pellet; $i = 2$: aggregate; i = 3: silica particle). Using the Bosanquet formula which describes the way to combine molecular and Knudsen diffusivities (Villermaux, 1993; Froment and Bischoff, 1990; Kapteijn and Moulijn, 1997), the Knudsen diffusivity equation (Satterfield, 1970; Kapteijn and Moulijn, 1997) and the approximation according to which the tortuosity factor is inversely proportional to the void fraction (Satterfield, 1970; Froment and Bischoff, 1990), the effective diffusivity can be developed and introduced in Eq. 2 so as to obtain the developed Eq. 3 of the Weisz modulus for one level $i$ characterized by its own bulk density $\rho_i$, its own characteristic size $L_i$, its own pore radius $r_{0,\,i}$ and its own void fraction $\epsilon_i$

$$\Phi_i = \frac{r \rho_i L_i^2}{C_{s,i}} \frac{\dfrac{1}{D_m} + \dfrac{1}{97 \times 10^{-3}\, r_{0,i} \sqrt{\dfrac{T}{M}}}}{\epsilon_i^2} \tag{3}$$

Values of $L_i$, $r_{0,\,i}$, $\rho_i$ and $\epsilon_i$ are estimated next.

*Estimation of the Characteristic Size $L_i$ at Each Level.* In Eqs. 1, 2 and 3, the characteristic size $L$ of an object is defined as the ratio between the volume and the surface of that object (Carberry, 1987; Villermaux, 1993; Froment and Bischoff, 1990; Kapteijn and Moulijn, 1997). Assimilating the three levels to spheres, which is a common approximation (Carberry, 1987; Villermaux, 1993; Froment and Bischoff, 1990), one obtains $L_i = d_i/6$ where $d_i$ is the diameter of the pellet, the aggregate, or the elementary silica particle assumed to be spherical. At level 1, since the catalysts pellets were sieved between $250 \times 10^{-6}$ and $500 \times 10^{-6}$ m, the value $d_1 = 500 \times 10^{-6}$ m will be used. It is decided to take this upper limit in order to obtain, via relation (Eq. 3), the maximum value of the Weisz modulus and therefore to be sure to detect diffusional limitations, if any. At level 2, the examination of Figures 2 and 3 indicate that $d_2 = 500 \times 10^{-9}$ m should be suitable as the upper limit for the aggregate diameter. At level 3, $d_3 = 20 \times 10^{-9}$ m (see Figure 3 and Results section). Values of $d_i$ for each level are given in Figure 6.

*Estimation of the Pore Radius $r_{0,i}$ Characteristic of Each Level.* Here again, values of $r_{0,\mathrm{i}}$ leading to maximum values of the Weisz modulus $\Phi_i$, that is to a maximum risk to encounter diffusional limitations, are evaluated at each level. Those values correspond to the minimum pore width which can be found at each level. The minimum pore width corresponding to level 1 (pellet), $w_{0,1}$, is the width of the smallest pores located between the aggregates of silica particles. According to Figures 2, 3 and 5, $50 \times 10^{-9}$ m seems to be a reasonable value for the minimum pore width at the level of the pellet and then $r_{0,1} = w_{0,1}/2 = 25\times10^{-9}$ m. According to the pore width distribution given in Figure 5, since the narrow micropore width at $w_0 = 0.8\times10^{-9}$ m is located inside the $20\times10^{-9}$ m elementary silica particles (level 3), the smallest width of pores at level 2, that is pores inside aggregates and outside silica particles, is the width just beyond that narrow distribution, that is $w_{0,2} = 2\times10^{-9}$ m. In consequence, $r_{0,2} = 1\times10^{-9}$ m. At level 3 (elementary silica particles), it is reasonable to take the center of the narrow distribution, that is $r_{0,3} = w_{0,3}/2 = 0.4\times10^{-9}$ m. Values of $w_{0,i}$ are described in Figure 6.

*Estimation of the Bulk Density $\rho_i$ Corresponding to Each Level.* As mentioned in the Results section, the bulk density of an object is the density of that object including pores. Therefore, in the present case, the bulk density $\rho_i$ corresponding to a given level $i$ is given by Eq. 4.

$$\rho_i = \frac{1}{\dfrac{1}{\rho_{\text{true}}} + V_i} \tag{4}$$

where $\rho_{\text{true}}$ is the true density of the material, that is, the density of the solid skeleton or the density excluding pores, and $V_i$ is the volume occupied by all the pores located inside the level $i$. The true density of the Pd-Ag xerogel catalyst is $\rho_{\text{true}} = 2.22\times10^3$ kg·m$^{-3}$ (see Results). The specific pore volume $V_1$ corresponding to level 1 (pellet) is the total cumulated pore volume given in Figure 5, that is, $V_1 = 6.25\times10^{-3}$ m$^3$·kg$^{-1}$, since the pellet contains all the pores. Hence, $\rho_1 =$ 149 kg·m$^{-3}$. According to the above limit width $w_{0,1} = 50\times10^{-9}$ m which corresponds to the width of the smallest pores located between the aggregates of silica particles, the specific pore volume $V_2$ corresponding to level 2 (aggregate) is the cumulated pore volume of pores whose width is smaller than $50\times10^{-9}$ m. Therefore, according to the pore width distribution given in Figure 5, $V_2 = 0.30\times10^{-3}$ m$^3$·kg$^{-1}$ and $\rho_2 =$ 1,327 kg·m$^{-3}$. In the same manner, the specific pore volume $V_3$ corresponding to level 3 ($SiO_2$ particle) is the cumulated pore volume of pores whose width is smaller than $2\times10^{-9}$ m. Therefore, $V_3 = 0.09\times10^{-3}$ m$^3$·kg$^{-1}$ and $\rho_3 = 1{,}861$ kg·m$^{-3}$. Values of $\rho_i$ are reminded in Figure 6.

*Estimation of the Void Fraction $\epsilon_i$ at Each Level..* Since, at a given level $i$, the diffusion under consideration is the diffusion between the core of the pores corresponding to that level and the surface of the following level, the void fraction $\epsilon_i$ corresponding to one level $i$ includes only pores characteristic of that level. That void fraction does not include the smaller pores contained in the following levels. In other words, the void fraction $\epsilon_i$ of a level $i$ is calculated assuming that the following levels are nonporous. Such a void fraction can be calculated by Eq. 5.

$$\epsilon_i = \frac{V_i - V_{i+1}}{\dfrac{1}{\rho_{\text{true}}} + V_i} \tag{5}$$

Values of $V_i$ and $\rho_{\text{true}}$ are given in the prior paragraph. Obviously, at level 3 (particle), $V_{i+1} = 0$. The values obtained are: $\epsilon_1 = 0.89$, $\epsilon_2 = 0.29$ and $\epsilon_3 = 0.16$ (Figure 6).

Before calculating the Weisz modulus $\Phi_i$ at each level by means of Eq. 3, $D_m$ and $C_{s,i}$ are needed. The molecular diffusivity $D_m$ of 1,2-dichloroethane has been calculated by means of the Chapman-Enskog equation (Satterfield, 1970; Bird et al., 1960) at 500, 573 and 623 K and results are given in Table 2. The 1,2-dichloroethane concentration in the bulk of the gas flow $C_b$ is calculated from the perfect gas law (Table 2). This bulk concentration is equal to the concentration $C_{s,1}$ at the surface of the catalyst pellets (level 1) only if there are no external diffusion limitations. This has been checked by means of the experimental test for external diffusion (Table 1 and Results section) and the calculation of the fraction of external resistance $f_e$ (Villermaux, 1993), which is much smaller than 1 in the temperature domain under consideration ($8\times10^{-6} \le f_e \le 2\times10^{-4}$). In consequence, $C_{s,1} = C_b$.

Since the surface concentration of 1,2-dichloroethane at the surface of the catalyst pellet is known, the Weisz modulus $\Phi_1$ at level 1 (pellet) can now be calculated through Eq. 3. By using values characteristic of level 1 (Figure 6) and values in Table 2, $\Phi_1$ is evaluated at 500, 573 and 623 K (Table 2). The low values obtained for $\Phi_1$ indicate that no limitation exists for the diffusion of 1,2-dichloroethane through the large pores from the surface of the pellet (level 1) to the surface of the aggregates (level 2). Therefore, there is no concentration gradient between the surface of the pellet and the surface of the aggregates. In consequence, $C_{s,2} = C_{s,1} = C_b$ and the Weisz modulus $\Phi_2$ at level 2 (aggregate) can be calculated. Low values are obtained (Table 2) which means that level 2 is also free from diffusional limitations and $C_{s,3} = C_{s,2} = C_{s,1} = C_b$, which allows to calculate $\Phi_3$ at level 3 (elementary silica particle). The very low values obtained for $\Phi_3$ (Table 2) demonstrate once again the absence of diffusional limitations inside the silica particles.

Let us mention that a kinetic study of 1,2-dichloroethane hydrodechlorination has been performed with the catalyst described in the present article (Heinrichs, 1999) and that an activation energy of 49 J mmol$^{-1}$ has been found. This value, which corresponds to the intrinsic activation energy of 1,2-dichloroethane dechlorination (Anju et al., 1972), confirms the absence of diffusional limitations which would falsify the kinetic data and then the activation energy. According to Eq. 3, such limitations would appear at level 1 at the highest temperature (623 K) if the pellet diameter $d_1$ was around $10^{-2}$ m, that is, a very large diameter comparable to the internal diameter of the reactor ($8\times10^{-3}$ m).

Let us make a brief comment here about diffusion inside the elementary silica particles (level 3). At this level, diffusion occurs in micropores whose width is $w_{0,3} = 0.8\times10^{-9}$ m, that is, a width which is in the order of magnitude of the molecule size. Such a width represents a boundary between two diffusion mechanisms: the Knudsen diffusion and the configurational diffusion (Weisz, 1973). This configurational regime was introduced by Weisz (1973) in the case of diffusion in zeolites whose pore width is close to the size of the diffusing molecules. Values of configurational diffusivity can be smaller than values of Knudsen diffusivity by several orders of magnitude. Therefore, if configurational diffusion is important in the micropores located inside the elementary silica particles (level 3), the real diffusivity of 1,2-dichloroethane could be much smaller than the one calculated by the Knudsen formula introduced in the Weisz modulus Eq. 3

(note that for such micropores, molecular diffusion does not take place anymore). In consequence, the Weisz modulus at level 3 $\Phi_3$ could be underestimated. However, even so, it is reasonable to think that the real value of $\Phi_3$ will still remain much smaller than 1 since values obtained considering only Knudsen diffusion are extremely low (Table 2).

The experimental test for internal mass transfer does not detect any diffusional limitations since the $ClCH_2$-$CH_2Cl$ conversion is pellet size independent (Table 1) (Kapteijn and Moulijn, 1997; L'Homme, 1970). Results of this test are then in agreement with the low values obtained for the Weisz modulus at the level of the pellet $\Phi_1$ (Table 2), indicating the absence of diffusional limitations in large pores between the aggregates of silica particles. However, the experimental test does not give any information about diffusion inside aggregates and elementary silica particles (levels 2 and 3) since the various crushing and sieving of the catalyst during that test modify the size of the pellets, that is, the size of level 1, but obviously neither the size of the aggregates nor the size of the silica particles. At levels 2 and 3, the calculation of the Weisz modulus only shows the absence of diffusional limitations.

## Conclusions

The analysis of the Pd-Ag low-density cogelled xerogel shows that this type of highly porous catalyst is composed of overlapping entities characterized by different textures and morphologies: elementary silica particles of about $20 \times 10^{-9}$ m and trapping the active Pd-Ag alloy crystallites are basic blocks which constitute larger aggregates which are several hundred of nanometers. Those aggregates constitute the macroscopic xerogel pellet. In order to reach the active sites, reactants have to diffuse through a continuous distribution of macro- and mesopores located in voids between aggregates of elementary $SiO_2$ particles and those elementary particles, and then through micropores of about $1 \times 10^{-9}$ m located inside the elementary $SiO_2$ particles. In order to study mass transfer in such a structure, it is suggested to consider it at three discrete levels with decreasing sizes: level 1: pellet; level 2: aggregate of silica particles; level 3: elementary silica particle containing an active Pd-Ag alloy crystallite. Each level is assumed to correspond to a pseudo-homogeneous medium with its own morphological and textural properties. At level 1 (pellet), only diffusion in large pores between aggregates is considered; at level 2 (aggregate), only diffusion in pores located inside the aggregates, but outside the $SiO_2$ particles, is considered; at level 3 (particle), only diffusion inside microporous $SiO_2$ particles is considered. In order to detect the presence of diffusional limitations at one or several level(s) inside the catalyst, the Weisz modulus $\Phi$, which compares the apparent reaction rate to the diffusion rate, is calculated at each level taking into account the intrinsic morphological and textural properties of the level considered. For the three levels, it is shown that $\Phi$ is much smaller than 1 which indicates that each level, and then the whole catalyst, is free from diffusional limitations.

To sum up, the structure of the catalyst studied here is such that, in order to reach the active sites, reactants (1,2-dichloroethane in the present case) must diffuse in pores of decreasing width (which makes mass transfer more difficult) located in entities of decreasing size (which makes mass transfer easier), increasing bulk density and decreasing void fraction (which makes mass transfer more difficult). Taken as a whole, those antagonistic effects lead to very small values of the Weisz modulus which indicates that a catalyst with such a "funnel" structure exhibits very good mass-transfer properties.

The kinetics and mechanism of 1,2-dichloroethane hydrodechlorination (HDC) over the Pd-Ag catalyst will be examined in another article.

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## Notation

$C_b$ = concentration in the bulk of the gas flow, $mmol \cdot m^{-3}$
$C_s$ = concentration at the external surface of a catalyst pellet, an aggregate of silica particles or an elementary silica particle, $mmol \cdot m^{-3}$
$d$ = diameter of a catalyst pellet, an aggregate of silica particles or an elementary silica particle, all assimilated to spheres, m
$D_e$ = effective diffusivity, $m^2 \cdot s^{-1}$
$D_m$ = molecular diffusivity, $m^2 \cdot s^{-1}$
$f_e$ = fraction of external resistance, dimensionless
$L$ = ratio between volume and external surface of a catalyst pellet, an aggregate of silica particles or an elementary silica particle, m
$M$ = molecular weight of 1,2-dichloroethane = $98.9596 \times 10^{-6}$, $kg \cdot mmol^{-1}$
$r$ = apparent reaction rate = apparent rate of 1,2-dichloroethane consumption, $mmol \cdot kg^{-1} \cdot s^{-1}$
$r_0$ = radius of a pore assimilated to a cylinder, m
$T$ = temperature, K
$V$ = volume occupied by all the pores inside a catalyst pellet, an aggregate of silica particles or an elementary silica particle, $m^3 \cdot kg^{-1}$
$w_0$ = pore width, m

### *Greek letters*

$\epsilon$ = void fraction, dimensionless
$\rho$ = bulk density of a catalyst pellet, an aggregate of silica particles or an elementary silica particle $kg \cdot m^{-3}$
$\rho_{true}$ = true density of the catalyst, $kg \cdot m^{-3}$
$\Phi$ = Weisz modulus, dimensionless

### *Subscripts*

$i$ = related to the $i^{th}$ level ($i = 1$: macroscopic catalyst pellet; $i = 2$: aggregate of silica particles; $i = 3$: elementary silica particle)

## Literature Cited

Alié, C., R. Pirard, A. J. Lecloux, and J.-P. Pirard "Preparation of Low-Density Xerogels Through Additives to TEOS-Based Alcogels," *J. Non-Cryst. Solids*, **246**, 216 (1999).

Anju, Y., I. Mochida, H. Yamamoto, A. Kato, and T. Seiyama, "The Dehalogenation of Haloalkanes on $SiO_2$-Supported Metals," *Bull. Chem. Soc. Jap.*, **45**, 2319 (1972).

Bird, R. B., W. E. Stewart, and E. N. Lightfoot, *Transport Phenomena*, Wiley, New York (1960).

Carberry, J. J., “Physico-Chemical Aspects of Mass and Heat Transfer in Heterogeneous Catalysis,” *Catalysis: Science and Technology*, J. R. Anderson and M. Boudart, eds., Vol. 8, Springer, Berlin, p. 131, (1987).

Delhez, P., B. Heinrichs, J.-P. Pirard, and J.-P. Schoebrechts, “Process for the Preparation of a Catalyst and its Use for the Conversion of Chloroalkanes into Alkenes Containing Less Chlorine,” U.S. Patent No. 6,072,096 (2000).

Emig, G., and R. Dittmeyer, “Simultaneous Heat and Mass Transfer and Chemical Reaction,” *Handbook of Heterogeneous Catalysis*, G. Ertl, H. Knözinger and J. Weitkamp, eds., Vol. 3, p. 1209, Wiley-VCH, Weinheim, Germany (1997).

Froment, G. F., and K. B. Bischoff, *Chemical Reactor Analysis and Design*, 2nd ed., Wiley, New York (1990).

Heinrichs, B., P. Delhez, J.-P. Schoebrechts, and J.-P. Pirard, “Palladium-Silver Sol-Gel Catalysts for Selective Hydrodechlorination of 1,2-Dichloroethane into Ethylene: I. Synthesis and Characterization, *J. Catal.*, **172**, 322 (1997a).

Heinrichs, B., F. Noville, and J.-P. Pirard, “Pd/$SiO_2$-Cogelled Aerogel Catalysts and Impregnated Aerogel and Xerogel Catalysts: Synthesis and Characterization,” *J. Catal.*, **170**, 366 (1997b).

Heinrichs, B., *L’Hydrodéchloration Sélective du 1,2-Dichloroéthane en Ethylène sur des Catalyseurs Pd-Ag/$SiO_2$*, PhD Thesis, Université de Liège, Liège (1999).

Heinrichs, B., F. Noville, J.-P. Schoebrechts, and J-P. Pirard, “Palladium-Silver Sol-Gel Catalysts for Selective Hydrodechlorination of 1,2-Dichloroethane into Ethylene: II. Surface Composition of Alloy Particles,” *J. Catal.*, **192**, 108 (2000).

Ito, L. N., A. D. Harley, M. T. Holbrook, D. D. Smith, C. B. Murchison, and M. D. Cisneros, “Processes for Converting Chlorinated Alkane Byproducts or Waste Products to Useful, Less Chlorinated Alkenes,” Patent Application No. WO 94/07827 (1994).

Kapteijn, F., and J. A. Moulijn, “Laboratory Catalytic Reactors: Aspects of Catalyst Testing,” *Handbook of Heterogeneous Catalysis*, G. Ertl, H. Knözinger and J. Weitkamp, eds., Vol. 3, p. 1359, Wiley-VCH, Weinheim, Germany (1997).

L’Homme, G. A., “La Contribution des Méthodes du Génie des Réactions Chimiques à la Conception des Mesures Cinétiques en Catalyse Hétérogène,” *Ind. Chim. Belge*, **35**, 291 (1970).

McKenna, T. F., D. Cokljat, R. Spitz, and D. Schweich, “Modelling of Heat and Mass Transfer During the Polymerisation of Olefins on Heterogeneous Ziegler Catalysts,” *Catal. Today*, **48**, 101 (1999).

Pajonk, G. M., “Aerogel Catalysts,” *Appl. Catal.*, **72**, 217 (1991).

Pajonk, G. M., A. V. Rao, B. M. Sawant, and N. N. Parvathy, “Dependence of Monolithicity and Physical Properties of TMOS Silica Aerogels on Gel Aging and Drying Conditions,” *J. Non-Cryst. Solids*, **209**, 40 (1997).

Rao, A. V., G. M. Pajonk, D. Haranath, and P. B. Wagh, “Effect of Glycerol on Monolithicity, Density, Microhardness and Sintering Temperature of TMOS Silica Aerogels,” *Microporous Mater.*, **12**, 63 (1997).

Rigacci, A., P. Achard, F. Ehrburger-Dolle, and R. Pirard, “Structural Investigation in Monolithic Silica Aerogels and Thermal Properties,” *J. Non-Cryst. Solids*, **225**, 260 (1998).

Rouquerol, J., D. Avnir, C. W. Fairbridge, D. H. Everett, J. H. Haynes, N. Pernicone, J. D. F. Ramsay, K. S. W. Sing, and K. K. Unger, “Recommendations for the Characterization of Porous Solids,” *Pure Appl. Chem.*, **66**, 1739 (1994).

Satterfield, C. N., *Mass Transfer in Heterogeneous Catalysis*, MIT Press, Cambridge (1970).

Schoebrechts, J.-P., and F. Janssens, “Method for Converting a Chlorinated Alkane into a Less Chlorinated Alkene,” Patent Application No. WO 96/16003 (1996).

Villermaux, J., *Génie de la Réaction Chimique - Conception et Fonctionnement des Réacteurs*, Lavoisier, Paris (1993).

Wakao, N., and J. M. Smith, “Diffusion in Catalyst Pellets,” *Chem. Eng. Sci.*, **17**, 825 (1962).

Weisz, P. B., “Zeolites-New Horizons in Catalysis,” *Chemtech*, 498 (1973).

Yamane, M., “Monolith Formation from the Sol-Gel Process, *Sol-Gel Technology for Thin Films, Fibers, Preforms, Electronics and Specialty Shapes*, L. C. Klein, ed., Noyes Publications, Park Ridge, NJ, p. 200 (1988).

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